ELECTROCHEMICAL INVESTIGATIONS OF Bi_2O_3 AND Bi_2O_3/X (X=ZnO, MnO_2) NANOCOMPOSITES WITH CARBON DERIVATIVES (rGO, MWCNT) IN REDOX ADDITIVE ELECTROLYTE FOR SUPERCAPACITOR APPLICATION

A SYNOPSIS

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1. Introduction

Energy and its uses are very important and unavoidable in the modern world. There are different types of energy including electrical, wind, ocean, hydropower, light, thermal, mechanical, nuclear, chemical energy, etc. The growing global population and the economy's expansion have combined to impact the next generation and burden the electrical infrastructure seriously. The three main fossil fuels used in today's world are coal, oil, and gas and they are non-renewable. The energy crisis is caused by many factors, including delays in power plant commissioning, underuse of renewable energy, insufficient energy distribution, serious accidents, natural disasters, overconsumption, poor infrastructure, energy waste, and an excess of people [1,2]. Although there are already alternative energy sources like wind turbines, solar cells, biomass plants, etc., are available, these technologies have some drawbacks, such as insufficient electrical energy storage. Due to the intermittent nature of this renewable energy, storage and supply are essential to maintaining a consistent supply of electricity to the devices. Modern electrical and electronic gadgets also require electrical supply and storage systems with a variety of energy and power capabilities to meet their requirements, which range from low to high. Therefore, it is necessary to develop a variety of unique energy delivery and storage solutions through the study of novel materials. A range of innovations in alternative energy storage devices, such as batteries, supercapacitors (SCs), and fuel cells, have been developed to address these needs [3,4].

SCs are widely used energy storage technologies that have extended cyclic lifetime, high power density, and high specific capacitance values. SCs are also known as ultracapacitors, which have a higher power density than conventional capacitors. They are used for a range of electrical purposes because the capacitors can be charged and discharged quickly [5,6]. SCs consist of two electrodes that are separated from one another and dipped in an electrolyte solution. The process of storing energy includes building up and releasing of electrical charges on two conducting plates that are significantly apart from one another. SCs are utilized in a wide range of industries, including aerospace and military, portable electric vehicles, high-speed electric vehicles, flexible electronics, uninterruptible power sources for electronic devices, and flexible electronics. The need for energy storage is constantly growing as a result of modern lifestyles, industrialization, and significant levels of carbon emissions. Due to the increasing importance of these technologies, scientists and engineers are keen to

increase their effectiveness and lower their costs. Furthermore, a single material cannot be adequate for a wide range of applications. As a result, a variety of materials need to be investigated for various types of application needs [7].

The most important characteristics of the SC electrodes are excellent charge-discharge, remarkable life span, and very high-power density with environmental friendliness. Based on their energy-storage method, the SCs can be divided into two categories: Electric double layer capacitor (EDLC) and pseudocapacitors (PC). Metal-based oxides/hydroxides/sulfides, conductive polymers, etc., have the feature of pseudocapacitance that allows fast faradic redox (reduction-oxidation) reactions at the electrode surface [8,9]. It possesses higher charge storage ability and power density. EDLC can be exhibited by carbon materials with a higher conductivity rate but with less charge storage ability. In most instances, the current capacity in both types is proportional to the electrode surface area that the access of electrolyte ions. The effectiveness of electrochemical energy devices is heavily reliant on electrolyte characteristics, electrode materials, rational device design, synthesis/functionalization processes, and so on.

The combination of EDLCs and PCs called hybrid capacitors (HCs) could be the wise choice to satisfy the energy needs of the future with better specific capacitance capabilities. However, the conventional metal oxides and mixed metal oxides could not have been the better alternatives and they should be enhanced optimally by chemical engineering. The carbon materials (in EDLCs) such as Multi-walled Carbon nanotubes (MWCNT), and reduced graphene oxide (rGO) have the potential to serve as the one-dimensional (1D) and two-dimensional (2D) structures, respectively for distributing and adorning high PC nanoparticles [10,11]. Due to physical interaction and/or chemical reactions at the surface or interface of the electrode and electrolyte, the structure of nanoparticles offers outstanding performances. In an experimental situation, pseudocapacitive materials can generate high capacitance values by chemical reactions, but they lack the necessary cyclic stability. Excellent cyclic stability and capacitance are features of electrical double-layer capacitive (EDLC) materials. HCs are generated by combining both to address these issues and improve performances. HCs have been developed to increase the device's power and energy density by the combination of EDLC and PC electrode materials utilized. The construction of a hybrid SC might take many different forms [12]. Similar to the electrode materials, electrolytes

also play a significant contribution in determining the SC's performances. Since the electrochemical performance of the electrolyte is based on its composition, the proper selection of electrolytes plays a critical role in the energy density and specific capacity values of the SCs. Commonly, aqueous solutions with inorganic salts, (like KOH, Na_2SO_4), organic liquids, etc., are used as the electrolytes. The electrochemical performance of these conventional electrolytes is enhanced by the addition of redox-active materials to the conventional electrolyte called redox additive electrolyte (RAE).

RAE is becoming increasingly important in SCs due to its ability to enhance energy density and stability while maintaining high power density. These electrolytes typically contain redox-active species, such as quinones, viologens, or ferrocyanide derivatives, which undergo reversible redox reactions at the electrode-electrolyte interfaces [13,14]. The incorporation of redox additives facilitates additional charge storage mechanisms beyond the traditional double-layer capacitance, leading to increased energy storage capacity. Moreover, redox reactions can mitigate issues associated with electrode surface passivation and electrolyte decomposition, thereby improving the cycling stability and lifetime of the SC. Furthermore, RAEs can extend the operational voltage window of the device, enabling higher energy density without sacrificing power density. Overall, the inclusion of RAEs offers a compelling strategy to enhance the performance and versatility of SCs, making them promising candidates for a wide range of energy storage applications. This research aims to prepare carbon-based mixed metal oxide electrodes and RAE for SC applications.

2. Literature Review

Various types of transition metal oxides, binary and ternary metal oxides, metal sulphides, metal ferrites, and metal oxide-based nanocomposites (NCs) were used as the electrode material for PC and hybrid SC applications. Among the various types of electrode materials, metal oxides stood out as the prominent electrode materials for SCs due to their high capacitance, chemical stability, and tunability, which facilitated the efficient energy storage and retrieval. A detailed literature survey on various metal oxide-based electrode materials in SCs were given below.

Elshahawy et al. [15] reported the fabrication of surface-engineered TiO_2 nanorod arrays anchored on carbon cloth using the Kapton tape-assisted hydrothermal method. Treatment of the sample surfaces resulted in significantly improved

conductivity and electrochemical performances of TiO_2. The surface-engineered TiO_2 nanorod arrays demonstrated a specific capacitance of approximately 57.62 $mFcm^{-2}$ at 10 mVs^{-1} in 2 M KOH and displayed an excellent rate capability of around 83% at 200 mVs^{-1}. Furthermore, these arrays exhibited an extended cycle life, retaining 91% of their initial capacitance after 10,000 charge/discharge cycles.

Jang et al. [16] reported the synthesis of porous cobalt oxide (Co_3O_4) nanocubes using a hydrothermal technique and explored their potential application in electrochemical SCs. The capacitive properties of the porous Co_3O_4 nanocubes electrode were scrutinized via cyclic voltammetry (CV) in 6 M KOH electrolyte and it exhibited the high specific capacitance of around 430.6 Fg^{-1} at a scan rate of 10 mVs^{-1}. The fabricated porous Co_3O_4 nanocubes electrode exhibited a capacity retention of up to approximately 85% after 1000 cycles, which highlighted its excellent structural stability. The obtained results suggested that the porous Co_3O_4 nanocubes exhibited high-quality characteristics, which were suitable for application as electrochemical SC electrodes.

Prasanna et al. [17] reported the synthesis of highly porous CeO_2 nanostructures suitable for SC applications, by combustion approach. The prepared CeO_2 electrodes were tested under 1M KOH electrolyte and it exhibited the initial specific capacitance of 134.6 Fg^{-1}, with superior cycling stability of 92.5% (after 1000 cycles at a constant current density of 1 Ag^{-1}). They revealed the potential suitability of the prepared CeO_2 electrodes as the efficient electrodes for SC devices.

Hroub et al. [18] reported Vanadium (V)-doped MgO nanoparticles as the electrode materials for solid-state SC applications. Electrochemical characteristics demonstrated that the innovative V-doped MgO material exhibited outstanding capacitance performance within the voltage range of 0 to 1 V and it achieved the specific capacitance of 50 Fg^{-1} at a scan rate of 10 mVs^{-1}. It also demonstrated a maximum energy density of 4.17 $Whkg^{-1}$, comparable to the values obtained from other symmetric SC configurations. The introduction of a booster material, such as carbon black, resulted in a significant increase in specific capacitance to 1200 Fg^{-1}.

Isacfranklin et al. [19] synthesized diverse vanadium oxide electrode materials by hydrothermal method. This investigation highlighted the superior electrochemical performance of cobalt vanadium oxide electrodes compared to nickel and bismuth

vanadium oxide counterparts. Exceptional results were observed, with a peak specific capacitance of 426.11 Fg^{-1} recorded in CV at 10 mVs^{-1} and 285.65 Fg^{-1} in Galvanostatic charge-discharge (GCD) at a current density of 0.5 mAg^{-1}. Moreover, the fabricated anode exhibited impressive capacitive retention of 83.64% over 5000 cycles.

Arasi et al. [20] synthesized nano-structured zinc vanadate, $Zn_3(VO_4)_2$ by simple co-precipitation method and calcined at 600 °C. The specific capacitance value for the prepared $Zn_3(VO_4)_2$ nanoparticles was 312 Fg^{-1} with high retention of about 90.7% after 5000 GCD cycles.

Kumar et al. [21] reported the synthesis of nickel ferrite ($NiFe_2O_4$) nanoparticles using a solution-based method, for potential application in SCs. The electrode for the SC was prepared by depositing $NiFe_2O_4$ nanoparticles onto a stainless-steel substrate through the drop-casting method. The $NiFe_2O_4$ nanoparticles exhibited a specific capacitance of approximately 120 Fg^{-1} in the SC application.

Shaheen et al. [22] employed a facile hydrothermal method to synthesize a novel electrode material composed of ZnO. The resulted phyto-fueled ZnO@PdO/Pd nanomaterial was then utilized in the fabrication of a SC electrode. Prepared electrode materials yielded a significant specific capacitance of 178 Fg^{-1} in KOH electrolyte solution. The charge-discharge data revealed that the prepared ZnO@PdO/Pd electrode possessed an energy density of 3.7 $Whkg^{-1}$ with a high-power density of 3718 Wkg^{-1}.

Vinayaraj et al. [23] synthesized $ZnWO_4$ and $ZnWO_4/SnO_2$ composites by solvothermal method. Synthesized $ZnWO_4/SnO_2$ composite demonstrated a specific capacitance of 56.7 Fg^{-1} at 1 mVs^{-1} and maintained 83% of cyclic stability at the end of 1000 cycles.

Kakani et al. [24] synthesized CuO@MnO_2 and CuO@MnO_2/N-MWCNT composites via hydrothermal and sonication-assisted methods. The composite electrodes of CuO@MnO_2/N-MWCNT displayed the electrochemical characteristics with the specific capacitance of 184 Fg^{-1} at a current density of 0.5 Ag^{-1} using 5 M KOH electrolyte. The electrodes demonstrated a cyclic retention of 98.5% over 5000 consecutive GCD cycles at 0.5 Ag^{-1}.

Wang et al. [25] reported an uncomplicated approach for producing ultrafine ruthenium oxides supported on diverse carbon-based substrates, including carbon

powders, carbon nanotubes, and rGO, which served as the exceptional electrode materials for SCs. Notably, due to their extremely fine particle size, the ruthenium oxides supported on carbon, carbon nanotubes, and rGO exhibited impressive specific capacitance values of 879.1 Fg^{-1}, 966.8 Fg^{-1}, and 1099.6 Fg^{-1}, respectively, at a current density of 0.5 Ag^{-1}. These materials maintain high specific capacitance levels of 98.4% (carbon support), 98.0% (carbon nanotube support), and 98.4% (rGO support) at a current density of 1 Ag^{-1}, which demonstrated excellent cycling stability.

Among the various metal oxides explored for SC applications, Bi_2O_3 stood out as a promising electrode material for SCs due to its earth abundance, dynamic redox pair, and environmentally friendly characteristics. The direct and rapid transition between the well-known redox states of Bi (III) and Bi (V), made it a novel and challenging electrode material for SCs. Despite its pseudocapacitive qualities, only a few studies explored the potential of Bismuth oxide in this regard. Additionally, substantial improvements were made in the architecture and redox durability of bismuth oxide.

Veeralakshmi et al. [26] synthesized a range of materials, including Bi_2O_3, Ag/Bi_2O_3, g-C_3N_4, and Ag/Bi_2O_3/g-C_3N_4 using the hydrothermal method. The materials were thoroughly characterized to assess their suitability for SC applications. The SC performance of the nanomaterials followed the order of Bi_2O_3 < g-C_3N_4 < Ag/Bi_2O_3/g-C_3N_4 < Ag/Bi_2O_3 with the Ag/Bi_2O_3 NC exhibited higher supercapacitance at 303 Fg^{-1}. This enhanced performance was attributed to the effective incorporation of silver doping in Bi_2O_3. Consequently, optimizing the rational design of such binary/ternary NCs was crucial for advancing further developments in SC applications.

Mbam et al. [27] synthesized and assessed the electrochemical performances of graphene oxide doped with bismuth oxide (Bi_2O_3@GO) and rGO doped with bismuth oxide (Bi_2O_3@rGO) in low concentrated (1.0 M) KOH electrolyte. Notably, the Bi_2O_3@rGO electrode exhibited superior performance with the specific capacitance value of 560 Fg^{-1} at a scan rate of 5 mVs^{-1}, along with the energy and power densities of 28 $Whkg^{-1}$ and 17 $kWkg^{-1}$, respectively. Furthermore, the electrode maintained an impressive 99% capacitance retention after 3000 GCD cycles.

Ali et al. [28] synthesized bismuth iron manganese oxide ($Bi_2Fe_2Mn_2O_{10}$) NCs by sol-gel/ultrasonic-assisted coprecipitation method with varied Mn concentrations,

referred as 10% Mn (BFM-1), 20% Mn (BFM-2), and 30% Mn (BFM-3). Electrochemical assessments revealed that BFM-3 displayed a specific capacitance of 664 Fg^{-1} in 6 M KOH at a current density of 0.35 Ag^{-1} using a three-electrode assembly. Additionally, an asymmetric SC was constructed utilizing BFM-3 and activated carbon (AC), which demonstrated a specific capacitance of 135 Fg^{-1} at a current density of 0.6 Ag^{-1} and delivered an energy density of 48 $Whkg^{-1}$ at a power density of 480 Wkg^{-1}. The device exhibited a capacitance retention of 93.3% over 5000 charge-discharge cycles.

The literature survey on metal oxide-based electrode materials suggested that the selection and composition of the electrode materials played a crucial role in SC performance. Conventional metal oxide-based electrode materials in SCs had drawbacks, such as limited energy density, low cyclic stability, a limited voltage window, high self-discharge rate, and environmental toxicity. As an alternative, Bi_2O_3-based materials acted as suitable electrode materials due to their high theoretical capacitance, various oxidation states, and low self-discharge rates, which helped to increase the energy density of the SCs. Additionally, the addition of other potential metal oxides could improve these characteristics through the additional benefits of the secondary metal oxides. On the other hand, the hybridization of the metal oxide-based electrode materials with carbon materials (composite materials) also improved SC performance due to the presence of both EDLC and PC mechanisms. Based on the literature, it was confirmed that the preparation of hybrid electrode materials composed of mixed metal oxides (combination of Bi_2O_3 and other potential metal oxides) and carbon derivatives, especially MWCNT and rGO, effectively improved the specific capacitance value, cycling stability, energy density, and power density of the SCs.

The effectiveness of SC in terms of electrochemical performance was influenced not only by the choice of electrode materials but also by the characteristics of the electrolytes used. The composition of electrolytes played a crucial role in determining their performance, and its modifications had a significant impact on the electrochemical performances. In particular, a promising strategy to enhance the redox capabilities and overall performance of electrolytes was the introduction of redox additives, also known as redox mediators, into conventional aqueous electrolytes. Recent studies in the literature suggested that the incorporation of redox additives into aqueous electrolytes led to improved electrochemical performances.

Senthilkumar et al. [14] provided insights into the importance of redox-mediated electrolytes in energy storage devices. The introduction of redox additives or mediators into the electrolytes improved the performance of SCs through redox processes occurred at the electrode-electrolyte interfaces. The primary advantage of this integration was its simplicity, safety, and cost-effectiveness, particularly in contrast to the preparation of diverse active electrode materials. Consequently, the identification of suitable redox additives or entities emerged as a pivotal focal point in the realm of SCs.

Park et al. [29] reported the enhanced electrolytic SC performances by the redox-active electrolyte (RAE) incorporation, which enhanced the energy density of SCs through the introduction of additional pseudocapacitances. It was derived from the incorporation of redox couples within the electrolyte. They employed a strategic design approach to create a nonaqueous redox-active electrolyte, primarily based on the relative positioning of the electrochemical stability window and the redox potential. Consequently, through a judicious pairing of the redox couple (decamethylcobaltocene/ decamethylcobaltocenium) and the supporting electrolyte (1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide dissolved in adiponitrile, they not only achieved the additional capacitance by the faradaic redox reactions from 21.3 Fg^{-1} to 57.1 Fg^{-1}, but also expanded the operating voltage window to nearly the entire electrochemical stability range of the supporting electrolyte (3.1 V). Carbon nanotube-based RAE utilization, demonstrated exceptional performances, including a significantly improved energy density (75.6 $Whkg^{-1}$), when compared to previously reported nonaqueous RAEs.

Nguyen et al. [13] documented an increase in the energy density of the assembled asymmetric supercapacitor (ASC) by incorporating a $NiCo(CO_3)$-$(OH)_2$ modified cathode, a Fe_2O_3/rGO modified anode, and a RAE based on $K_3[Fe(CN)_6]$ + KOH. The cathode material, synthesized through hydrothermal methods, demonstrated an impressive specific capacitance of 3248.9 Fg^{-1} at 1 Ag^{-1} under a RAE of 0.06 M $K_3[Fe(CN)_6]$ in 3 M KOH. At a power density of 825 Wkg^{-1}, the constructed ASC delivered a higher energy density of 84.1 $Whkg^{-1}$.

Sundriyal et al. [30] reported the SC performance of a rGO/TiO_2 electrode in combination with a RAE (0.2 M $K_3[Fe(CN)_6]$ in 1 M Na_2SO_4). The rGO/TiO_2 electrode

and the optimized RAE achieved the highest specific capacitance of 1565 Fg^{-1} at a current density of 3 Ag^{-1}. The fabricated symmetrical SC device using rGO/TiO_2 achieved specific capacitance value of 204.5 Fg^{-1} at a current density of 1.5 Ag^{-1}. The device also yielded the energy density of 15.5 $Whkg^{-1}$, power density of 1.1 $kWkg^{-1}$ and a long-term cyclic stability of 87% after 1000 GCD cycles.

Ramachandran et al. [31] described the synthesis of composites based on cerium metal-organic frameworks (Ce-MOF/GO and Ce-MOF/CNT) through a wet chemical approach. The electrochemical characteristics of the resulted composites were investigated and compared in the electrolytes of 3 M KOH and 3 M KOH + 0.2 M $K_3Fe(CN)_6$. Prepared Ce-MOF/GO composite exhibited the enhanced electrochemical performances in the presence of 0.2 M $K_3Fe(CN)_6$ redox additives added to 3 M KOH, which exhibited the maximum specific capacitance of 2221 Fg^{-1} and an energy density of 111 $Whkg^{-1}$ at a current density of 1 Ag^{-1}.

Arunpandiyan et al. [32] reported the electrochemical performances of the CeO_2 nanoparticles (NPs) decorated MnO_2 nanorods (NRs) in RAE. They prepared pure CeO_2 NPs and MnO_2 NRs by the hydrothermal method, and decorated the prepared CeO_2 NPs over the MnO_2 NRs through a facile ultrasonic technique. The electrochemical performances of the CeO_2 NPs decorated MnO_2 NRs had been studied in 3 M aqueous KOH electrolyte and 0.2 M $K_4[Fe(CN)_6]$ added 3 M KOH electrolyte, and it exhibited the superior capacitance of 1058.2 Fg^{-1} in 0.2 M $K_4[Fe(CN)_6]$ added 3 M KOH electrolyte.

Hariharan et al. [33] reported the electrochemical performances of the Zinc oxide/Nickel oxide loaded MWCNT (ZnO/NiO@MWCNT - ZNC) under different electrolytes. ZNC NCs were successfully synthesized by a simple one-step hydrothermal method and calcinated at 500 °C. ZNC NCs modified working electrode's performances were tested using different electrolytes, such as 1 M KOH, 1 M KOH + 0.1 M $K_4[Fe(CN)_6]$, 1 M Na_2SO_4 and 1 M Na_2SO_4 + 0.1 M $K_4[Fe(CN)_6]$. Among these electrolytes, ZNC NCs modified working electrode possessed the superior electrochemical performance with the specific capacitance value of 1988.8 Fg^{-1} under 0.1 M $K_4[Fe(CN)_6]$ added 1 M Na_2SO4 aqueous electrolyte and achieved a superior specific capacitance retention of 97.2 % after 2000 GCD cycles. The fabricated asymmetrical type SCs possessed the superior energy and power densities of 43.59

$Whkg^{-1}$ and 4000 Wkg^{-1}, respectively under the freshly prepared redox additives added Na_2SO_4 aqueous electrolyte.

The literature reviews proved that the conventional electrolytes, such as, KOH and Na_2SO_4, were inadequate to meet the requisites of the advanced SCs due to their, poor charge transfer ability and limited redox reactions. It explored the necessity of advanced electrolytes with superior characteristics, such as, higher conductivity, and redox-active sites for additional redox reactions. Incorporation of redox additives was the potential remedy for these issues. Particularly, RAE containing 0.1 M $K_3Fe(CN)_6$ in 1 M KOH emerged as a highly practical and fitting choice for SC applications. These RAE was effective to enhance the cycling stability, as well as to improve the energy density, power density, and specific capacitance values of the SCs.

3. Objective

The objective of this work was to fabricate a stable and high-performance SCs using Bi_2O_3 based NCs as the electrode materials and RAE. It was accomplished through the following steps,

- Synthesis and characterization of pure Bi_2O_3, Bi_2O_3/X, Bi_2O_3/X:rGO, and Bi_2O_3/X:MWCNT (X – ZnO and MnO_2) NCs
- Fabrication of working electrodes and SCs using the prepared NCs.
- Electrochemical investigations on the fabricated working electrodes and SCs using 1 M KOH electrolyte and 0.1 M $K_4[Fe(CN)_6]$ added 1 M KOH-based RAE.

4. Research Problem

The major issues associated with SCs in real time applications were,

- The SCs typically have lower energy density, low operating voltage, higher self-discharge rate, energy storage capacity and environmental impact of the materials used, compared to batteries.
- The pure and binary metal oxides used in SC electrodes were inadequate to produce superior redox reactions and less stable
- The metal oxides and their derivatives used in SCs have lower conductivity and charge transfer rate, which limited their potential applications.

- The conventional electrolyte only acted as a charge transport medium between the electrodes, which reduced the overall performance of the SC.
- The electrode's and electrolyte's performances need to be improved to achieve superior SC performances with high power density, improved operating potential, superior charge storage capacity with minimal discharge rate.

5. Organization of Thesis

The research problem discussed earlier was investigated and analyzed through various analytical techniques. The work done in this research was outlined in Figure 1.

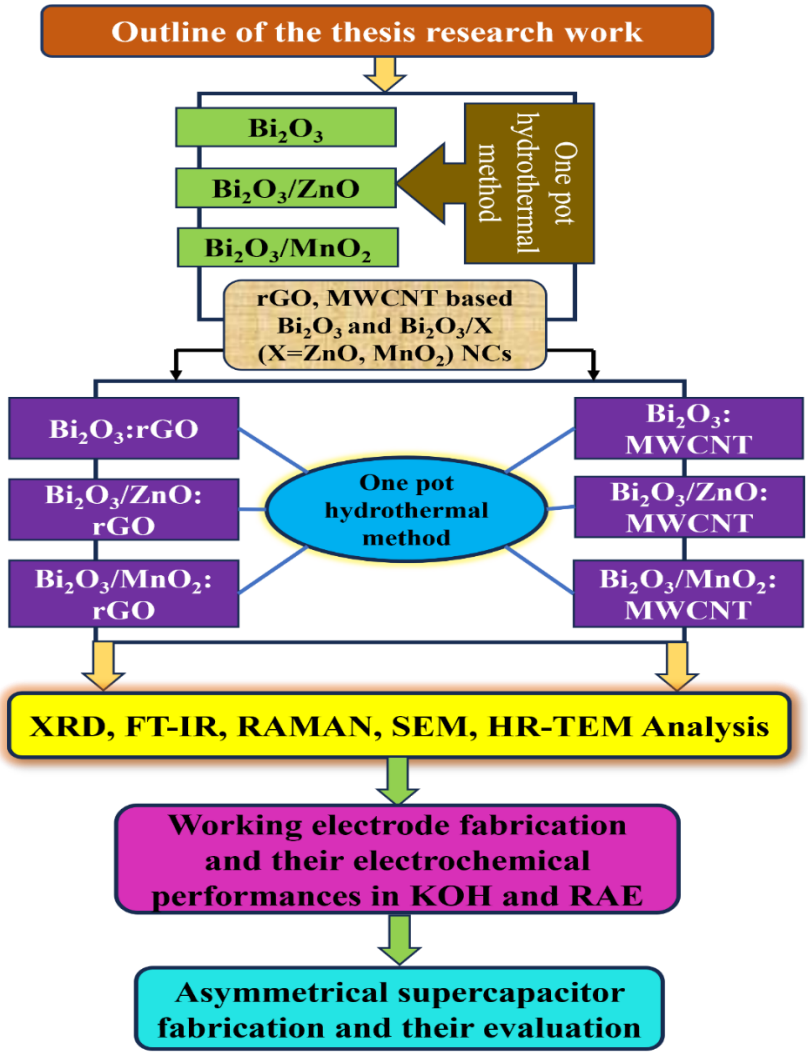

Figure 1 Schematic illustration of the outline of thesis research work

The contents planned in thesis were as follows:

Chapter 1 discussed the introduction and overview of energy storage technologies, particularly electrochemical energy storage systems, and their various

types, such as, batteries, capacitors, redox flow batteries, fuel cells, and SCs. This chapter discussed the importance of SCs and their classifications, such as, electric EDLCs, PCs, and hybrid supercapacitors (HCs). It also discussed the applications and parts of a SC. A brief description about the types of materials used in electrodes and their importance for SCs had been included in this chapter. In addition, the types of electrolytes used in SCs and their necessity were also provided.

Chapter 2 discussed the literature survey of the current research work. The characteristic requirements of a SC to meet the current trend were listed. The types of materials used for electrode fabrication and their results were discussed. Particularly bismuth oxide-based mixed metal oxides and with carbon-based NCs had been reviewed to identify the research gap and area of interest for further investigation. The role of conventional electrolytes and their types used in the SCs were reviewed. The steps involved in the performance enhancement of conventional electrolytes and the significance of redox additive-based electrolytes were discussed. The performance of hybrid electrode and RAEs combination and their significance were provided. The research described here attempts to improve specific capacitance and cyclic stability while simultaneously enhancing energy density and power density of the envisioned NCs. Finally, the scope and outline of the thesis research work were listed precisely.

Chapter 3 discussed the experimental part of the research work. A detailed list of chemical reagents and characterization techniques used in the research work was illustrated. This chapter discussed the synthesis of all Bi_2O_3, Bi_2O_3/ZnO, Bi_2O_3/MnO_2, Bi_2O_3:rGO, Bi_2O_3/ZnO:rGO, Bi_2O_3/MnO_2:rGO, Bi_2O_3:MWCNT, Bi_2O_3/ZnO:MWCNT, and Bi_2O_3/MnO_2:MWCNT NCs. The preparation method used for the synthesis of conventional KOH and RAE were described. Fabrication of working electrodes and SCs based on the prepared NCs through doctor blade method were discussed. The characterization techniques, such as, X-ray diffraction analysis (XRD), Fourier Transform Infra-Red (FT-IR) spectroscopy, Raman spectroscopy, Scanning Electron Microscopy (SEM) analysis, Energy dispersive X-ray spectroscopy (EDS), Elemental mapping, High-resolution transmission electron microscopy (HR-TEM) analyses, used for the analysis of physical, chemical, structural properties of the prepared NCs were elaborated. The electrochemical techniques, such as Cyclic Voltammetry (CV), Galvanostatic Charge-Discharge (GCD), and Electrochemical Impedance Spectroscopy (EIS) techniques, used for the evaluations of the fabricated

working electrodes and SCs were described. This chapter also discusses the fundamentals, functions, and roles behind the aforementioned characterization techniques.

Chapter 4 discussed the electrochemical investigation of pure Bi_2O_3, and Bi_2O_3/X (X= ZnO, MnO_2) NCs under RAE. Prepared pure Bi_2O_3, and Bi_2O_3/X (X= ZnO, MnO_2) NCs were analytically characterized with XRD, FT-IR, and Raman analyses, to reveal the structural and functional group characteristics. The morphological and elemental information were studied by the SEM and EDS analyses. The electrochemical performances of the fabricated working electrodes and devices were evaluated using CV, GCD, and EIS analyses. The prepared electrodes, such as, BO, BZ, and BM electrodes delivered superior electrochemical performances with the highest C_{sp} values of 93.7, 1189.6, and 217.5 Fg^{-1}, respectively in RAE, compared to KOH (80.8, 111.4, and 103.6 Fg^{-1}). Similarly, the fabricated BO, BZ, and BM SCs showed better performances in RAE. Specifically, BO, BZ, and BM SCs exhibited an outstanding E_d values of 1.02 $Whkg^{-1}$, 9.2 $Whkg^{-1}$, and 7.99 $Whkg^{-1}$, respectively, and the P_d values of 250 Wkg^{-1}, 1680 Wkg^{-1}, 900 Wkg^{-1}, respectively in KOH. Furthermore, the addition of redox additives further improved their performances to 3.65 $Whkg^{-1}$, 29.5 $Whkg^{-1}$, 14.0 $Whkg^{-1}$, respectively and 420 Wkg^{-1}, 1820 Wkg^{-1}, 1540 Wkg^{-1}, respectively (in RAE). Remarkably, BO, BZ and BM SCs displayed the long-term stabilities with 73.65%, 81.20%, 78.90% of capacitance retention in RAE even after 5000 GCD cycles.

Chapter 5 discussed the enhanced SC performances of Bi_2O_3 and Bi_2O_3/X (X= ZnO, MnO_2) with rGO NCs under RAE. Hydrothermally synthesized Bi_2O_3:rGO (BOR), Bi_2O_3/ZnO:rGO (BZR), and Bi_2O_3/MnO_2:rGO (BMR) NCs' structural, functional, vibrational, morphological, and electrochemical properties had been studied. The electrochemical capabilities of BOR, BZR, and BMR-modified electrodes and SCs were tested under aqueous KOH and RAE electrolytes. The BOR, BZR, and BMR electrodes exhibited the maximum C_{sp} values of 29.6, 31.14, and 31.65 Fg^{-1} in 1M KOH electrolyte and these values were improved to 200, 633, and 987 Fg^{-1}, respectively by using RAE. The fabricated SCs revealed the highest E_d and P_d values of 11.03 $Whkg^{-1}$ and 1680 Wkg^{-1} (BOR SCs), 34.20 $Whkg^{-1}$, and 1890 Wkg^{-1} (BZR SCs), 16.08 $Whkg^{-1}$ and 2800 Wkg^{-1} (BMR SCs), respectively under RAE, whereas these devices possessed only 2.96 $Whkg^{-1}$ and 356 Wkg^{-1}, 15.3 $Whkg^{-1}$ and 1750

Wkg^{-1}, 9.4 $Whkg^{-1}$ and 2100 Wkg^{-1}, respectively under KOH. The combined effect of rGO inclusion in electrode materials, and redox additive addition in electrolyte, were responsible for the improved C_{sp} values, E_d, and P_d values of the prepared SCs.

Chapter 6 discussed the redox additives-dependent SC performance of MWCNT incorporated Bi_2O_3, and Bi_2O_3/X (X= ZnO, MnO_2) NCs. The structural, functional group, and morphological characteristics of the prepared The Bi_2O_3:MWCNT (BOM), Bi_2O_3/ZnO:MWCNT (BZM), and Bi_2O_3/MnO_2:MWCNT (BMM) NCs were revealed by the XRD, FT-IR, Raman, SEM, and HR-TEM analyses. The electrochemical capabilities of BOM, BZM, and BMM electrodes and SCs were tested under KOH and RAE electrolytes. The prepared BOM, BZM, and BMM electrodes delivered the highest C_{sp} values of 583.2, 3038.9, and 1768.3 Fg^{-1}, respectively in RAE, and these values were very high compared to KOH electrolytes (143.3 Fg^{-1}, 171.8 Fg^{-1}, and 166.3 Fg^{-1}). On the other hand, the fabricated BOM, BZM, and BMM SCs exhibited the highest E_d and P_d values of 17.1 $Whkg^{-1}$ and 1520 Wkg^{-1} (BOM SCs), 40.8 $Whkg^{-1}$ and 2100 Wkg^{-1} (BZM SCs), 21.2 $Whkg^{-1}$ and 1400 Wkg^{-1} (BMM SCs) respectively under RAE, whereas these devices possessed only 5.5 $Whkg^{-1}$ and 720 Wkg^{-1}, 9.4 $Whkg^{-1}$ and 1800 Wkg^{-1}, 8.2 $Whkg^{-1}$ and 340 Wkg^{-1}, respectively under KOH. The prepared BOM, BZM, and BMM electrodes and SCs exhibited the highest C_{sp}, cyclic stability, P_d, and E_d values compared to other fabricated electrodes and devices (BO, BZ, BM, BOR, BZR, and BMR electrodes and SCs) in both the KOH and RAE. It revealed that the inclusion of MWCNT in electrode materials and the addition of redox additives in conventional electrolyte, improved the electrochemical characteristics for SC applications.

Chapter 7 concluded the overall summary of all the research works described in the dissertation. In detail, the significance of hybrid electrodes, RAEs, and their combined effect was clearly illustrated. Furthermore, the effects of rGO and MWCNT loaded on the Bi_2O_3, and Bi_2O_3/X (X= ZnO, MnO_2) NCs and their electrochemical performances were reported. Through the knowledge acquired from the dissertation, an effective future work plan to attain real-time application was also enlisted.

References

[1]. R. Kandpal, R. Singh, Renewable Energy Sources – A Review, *ECS Transactions*, **107** (1) (2022), 8133–8140

[2]. S. Koohi-Fayegh, M.A. Rosen, A review of energy storage types, applications and recent developments, *Journal of Energy Storage*, **27** (2020), 101047

[3]. Y.K. Sun, Promising All-Solid-State Batteries for Future Electric Vehicles, *ACS Energy Letters*, **5** (10) (2020), 3221–3223

[4]. L. Fan, Z. Tu, S.H. Chan, Recent development of hydrogen and fuel cell technologies: A review, *Energy Reports*, **7** (2021), 8421–8446

[5]. J. Libich, J. Máca, J. Vondrák, O. Čech, M. Sedlaříková, Supercapacitors: Properties and applications, *Journal of Energy Storage*, **17** (2018), 224–227

[6]. P. Sharma, V. Kumar, Current Technology of Supercapacitors: A Review, *Journal of Electronic Materials*, **49** (6) (2020), 3520–3532

[7]. A. Muzaffar, M.B. Ahamed, K. Deshmukh, J. Thirumalai, A review on recent advances in hybrid supercapacitors: Design, fabrication and applications, *Renewable and Sustainable Energy Reviews*, **101** (2019), 123–145

[8]. C. Costentin, J.M. Savéant, Energy storage: Pseudocapacitance in prospect, *Chemical Science*, **10** (22) (2019), 5656–5666

[9]. S. Fleischmann, J.B. Mitchell, R. Wang, C. Zhan, D.E. Jiang, V. Presser, V. Augustyn, Pseudocapacitance: From Fundamental Understanding to High Power Energy Storage Materials, *Chemical Reviews*, **120** (14) (2020), 6738–6782

[10]. L. Zhao, W. Jian, X. Zhang, F. Wen, J. Zhu, S. Huang, J. Yin, K. Lu, M. Zhou, W. Zhang, X. Qiu, Multi-scale self-templating synthesis strategy of lignin-derived hierarchical porous carbons toward high-performance zinc ion hybrid supercapacitors, *Journal of Energy Storage*, **53** (2022), 105095

[11]. S.W. Bokhari, A.H. Siddique, P.C. Sherrell, X. Yue, K.M. Karumbaiah, S. Wei, A. V. Ellis, W. Gao, Advances in graphene-based supercapacitor electrodes, *Energy Reports*, **6** (2020), 2768–2784

[12]. R. Kumar, S. Sahoo, W.K. Tan, G. Kawamura, A. Matsuda, K.K. Kar, Microwave-assisted thin reduced graphene oxide-cobalt oxide nanoparticles as hybrids for electrode materials in supercapacitor, *Journal of Energy Storage*, **40** (2021), 102724

[13]. V.T. Nguyen, J.M. Ting, A Redox-Additive Electrolyte and Nanostructured Electrode for Enhanced Supercapacitor Energy Density, *ACS Sustainable Chemistry and Engineering*, **8** (49) (2020), 18023–18033

[14]. S.T. Senthilkumar, R.K. Selvan, J.S. Melo, Redox additive/active electrolytes: A novel approach to enhance the performance of supercapacitors, *Journal of Materials Chemistry A*, **1** (40) (2013), 12386–12394

[15]. A.M. Elshahawy, S.M. Elkatlawy, M.S. Shalaby, C. Guan, J. Wang, Surface-Engineered TiO_2 for High-Performance Flexible Supercapacitor Applications, *Journal of Electronic Materials*, **52** (2) (2023), 1347–1356

[16]. G.S. Jang, S. Ameen, M.S. Akhtar, H.S. Shin, Cobalt oxide nanocubes as electrode material for the performance evaluation of electrochemical supercapacitor, *Ceramics International*, **44** (1) (2018), 588–595

[17]. K. Prasanna, P. Santhoshkumar, Y.N. Jo, I.N. Sivagami, S.H. Kang, Y.C. Joe, C.W. Lee, Highly porous CeO_2 nanostructures prepared via combustion synthesis for supercapacitor applications, *Applied Surface Science*, **449** (2018), 454–460

[18]. A. Hroub, M.H. Aleinawi, M. Stefan, M. Mihet, A. Ciorita, F. Bakan-Misirlioglu, E. Erdem, A.M. Rostas, Vanadium-doped magnesium oxide nanoparticles as electrodes in supercapacitor devices, *Journal of Alloys and Compounds*, **958** (2023), 170442

[19]. M. Isacfranklin, C. Deepika, G. Ravi, R. Yuvakkumar, D. Velauthapillai, B. Saravanakumar, Nickel, bismuth, and cobalt vanadium oxides for supercapacitor applications, *Ceramics International*, **46** (18) (2020), 28206–28210

[20]. S. Ezhil Arasi, P. Devendran, R. Ranjithkumar, S. Arunpandiyan, A. Arivarasan, Electrochemical property analysis of zinc vanadate nanostructure for efficient supercapacitors, *Materials Science in Semiconductor Processing*, **106** (2020), 104785

[21]. R. Kumar, R. Kumar, P. Kumar Sahoo, M. Singh, A. Soam, Synthesis of nickel ferrite for supercapacitor application, *Materials Today: Proceedings*, **67** (2022), 1001–1004

[22]. I. Shaheen, K.S. Ahmad, C. Zequine, R.K. Gupta, A.G. Thomas, M.A. Malik, Facile ZnO-based nanomaterial and its fabrication as a supercapacitor electrode: synthesis, characterization and electrochemical studies, *RSC Advances*, **11** (38) (2021), 23374–23384

[23]. S. Vinayaraj, K. Brijesh, P.C. Dhanush, H.S. Nagaraja, $ZnWO_4/SnO_2$ composite for supercapacitor applications, *Physica B: Condensed Matter*, **596** (2020), 412369

[24]. V. Kakani, S. Ramesh, H.M. Yadav, C. Bathula, P.K. Basivi, R.R. Palem, H.S. Kim, V.R. Pasupuletti, H. Lee, H. Kim, Hydrothermal synthesis of $CuO@MnO_2$ on nitrogen-doped multiwalled carbon nanotube composite electrodes for supercapacitor applications, *Scientific Reports*, **12** (1) (2022), 12951

[25]. P. Wang, H. Liu, Y. Xu, Y. Chen, J. Yang, Q. Tan, Supported ultrafine ruthenium oxides with specific capacitance up to 1099 Fg^{-1} for a supercapacitor, *Electrochimica Acta*, **194** (2016), 211–218

[26]. S. Veeralakshmi, S. Kalaiselvam, R. Murugan, P. Pandurangan, S. Nehru, S. Sakthinathan, T.W. Chiu, An approach to develop high performance supercapacitor using Bi_2O_3 based binary and ternary nanocomposites, *Journal of Materials Science: Materials in Electronics*, **31** (24) (2020), 22417–22426

[27]. S.M. Mbam, R.M. Obodo, O.O. Apeh, A.C. Nwanya, A.B.C. Ekwealor, N. Nwulu, F.I. Ezema, Performance evaluation of Bi_2O_3@GO and Bi_2O_3@rGO composites electrode for supercapacitor application, *Journal of Materials Science: Materials in Electronics*, **34** (18) (2023), 1405

[28]. D. Ali, F. Ashiq, I. Muneer, H.M. Fahad, A. Waheed, M.Z. Butt, R. Ahmad, M.F.M.R. Wee, Bismuth iron manganese oxide nanocomposite for high performance asymmetric supercapacitor, *Electrochimica Acta*, **464** (2023), 142863

[29]. J. Park, Y.E. Yoo, L. Mai, W. Kim, Rational Design of a Redox-Active Nonaqueous Electrolyte for a High-Energy-Density Supercapacitor Based on Carbon Nanotubes, *ACS Sustainable Chemistry and Engineering*, **7** (8) (2019), 7728–7735

[30]. S. Sundriyal, V. Shrivastav, M. Sharma, S. Mishra, A. Deep, Significantly enhanced performance of rGO/TiO_2 nanosheet composite electrodes based 1.8 V symmetrical supercapacitor with use of redox additive electrolyte, *Journal of Alloys and Compounds*, **790** (2019), 377–387

[31]. R. Ramachandran, W. Xuan, C. Zhao, X. Leng, D. Sun, D. Luo, F. Wang, Enhanced electrochemical properties of cerium metal-organic framework based composite electrodes for high-performance supercapacitor application, *RSC Advances*, **8** (7) (2018), 3462–3469

[32]. S. Arunpandiyan, S. Vinoth, A. Pandikumar, A. Raja, A. Arivarasan, Decoration of CeO_2 nanoparticles on hierarchically porous MnO_2 nanorods and enhancement of supercapacitor performance by redox additive electrolyte, *Journal of Alloys and Compounds*, **861** (2021), 158456

[33]. G. Hariharan, S. Arunpandiyan, V. Shanmugapriya, S. Bharathi, M. Babu, B. Selvakumar, A. Arivarasan, Role of various redox additive electrolytes on the electrochemical performances of mixed metal oxide loaded multiwalled carbon nanotube based supercapacitors, *Journal of Energy Storage*, **57** (2023), 174164

List of Publications

1. **V. Shanmugapriya**, S. Arunpandiyan, G. Hariharan, S. Bharathi, B. Selvakumar, A. Arivarasan, Enhanced electrochemical performance of mixed metal oxide (Bi_2O_3/ZnO) loaded multiwalled carbon nanotube for high-performance asymmetric supercapacitors, *Journal of Energy Storage*, **55** (2022), 105739.
2. **V. Shanmugapriya**, G. Hariharan, S. Ganapathy, S. Bharathi, A. Arivarasan, Unleashing the Potential: Augmented Supercapacitor Performance of Bi_2O_3 /MnO_2@MWCNT Nanocomposites with Redox Additive Electrolyte, *ACS Energy & Fuels*, **37** (24) (2023), 19925-19938.
3. **V. Shanmugapriya**, S. Arunpandiyan, G. Hariharan, S. Bharathi, B. Selvakumar, A. Arivarasan, Enhanced Supercapacitor Performance of ZnO/SnO_2:rGO Nanocomposites under Redox Additive Electrolyte, *Journal of Alloys and Compounds*, **935** (2023), 167994.
4. **V. Shanmugapriya**, G. Hariharan, S. Arunpandiyan, M. Babu, S. Bharathi, B. Selvakumar, A. Arivarasan, Redox additives dependent supercapacitor performances of ZnO/SnO_2@MWCNT nanocomposites, Diamond and Related Materials, **140** (2023), 110482.